# IMPACT OF BRACKISH GROUNDWATER AND TREATED WASTEWATER ON SOIL CHEMICAL AND MINERALOGICAL PROPERTIES

#### A Thesis

by

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Submitted to the Office of Graduate and Professional Studies of Texas A&M University in partial fulfillment of the requirements for the degree of

# MASTER OF SCIENCE

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May 2018

Major Subject: Water Management and Hydrological Science

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#### **ABSTRACT**

The purpose of this study was to assess the impact of non-traditional water irrigation on the chemical and mineralogical properties of the calcareous clayey Angelo soil from West Texas. The exponential rise in population and climate change is leading to further increase in freshwater (FW) depletion, treated wastewater (TWW) and brackish groundwater (BGW) thus offer the possibility of attractive alternative water resources for irrigated agriculture.

To address the differences between TWW and BGW, water samples were collected and analyzed. The water samples were analyzed for salt and nutrient content. Soil samples from three horizons (Ap, A, and B) were obtained from three different fields: Rainfed (RF), BGW irrigated, and TWW irrigated. Soil was analyzed for texture, salinity, sodicity, and carbon content. Clay mineralogy of the three different fields was analyzed using the B-horizons.

TWW is slightly saline compared to the moderately saline BGW. Although, the exchangeable sodium percentage (ESP), sodium adsorption ratio (SAR), and electroconductivity (EC) have marginally increased compared to RF, however all the values of interest (SAR<13, ESP<15, pH<8.5, and EC<4) were low indicating no sodicity nor salinity problems. Smectite, illite, and kaolinite were identified in the three B-horizon samples by XRD. Overall, there was no major changes in the soil observed, which deems TWW and BGW as viable replacements for FW in arid and semi-arid regions.

# **DEDICATION**

I dedicate this work to my parents, significant other, family, and my friends for all their encouragement and support throughout my journey to obtain this degree.

#### **ACKNOWLEDGEMENTS**

I would like to acknowledge and thank my committee chair, Dr. Rabi Mohtar, and my committee members, Dr. Paul Schwab, Dr. Youjun Deng, Dr. Anish Jantrania, and Dr. Clyde Munster, for their commitment, guidance and continued support throughout the course of my research and studies. I also would express my appreciation to Dr. Amjad Assi for his help and advising efforts. In addition, I would like to specially thank Mr. Mathew Wilde for allowing access to his land for soil and water sampling. Without his permission and cooperation, this research would not have been possible.

I would like to acknowledge WEF Nexus Research Group members and their support and help. Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

Finally, thanks to my parents for their encouragement and to my significant other for her patience, support, and love.

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# **Funding Sources**

This research was funded by the Water-Energy-Food Nexus Initiative (WEFNI) at Texas A&M University.

# **NOMENCLATURE**

ACFT Acre-feet

BGW Brackish Groundwater

BOD<sub>5</sub> Biological Oxygen Demand

CEC Cation Exchange Capacity

COD Chemical Oxygen Demand

EC Electroconductivity

ESP Exchangeable Sodium Percentage

ESR Exchangeable Sodium Ratio

FAO Food and Agriculture Organization

FF Filter-flush

FW Freshwater

GW Groundwater

RF Rainfed

SAR Sodium Adsorption Ratio

TDS Total Dissolved Solids/Salts

TOC Total Organic Carbon

TSS Total Suspended Solids

TWDB Texas Water Development Board

TWW Treated Wastewater

WW Wastewater

XRD X-Ray Diffraction

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#### 1. INTRODUCTION

# 1.1 Background

Water scarcity is one of the major threats facing humanity with the increasing competition for resources resulting from the growth in population. The demand for water has increased with the requirements of the different sectors to supply the fundamental human needs. Globally, the agriculture sector consumes the greatest amount of water 70% compared to 10% for domestic use and 20% for industry (Food and Agriculture Organization (FAO), 2010). The impacts from climate change add to the burden of the deficit between demand and supply for water. In 2030, with a "business as usual model", the projected global water gap (shortage) will be 40% and one third of the population will be living in water stressed regions (WEF-WRG, 2012). The projected increase in frequencies of drought conditions (Intergovernmental Panel on Climate Change (IPCC), 2013) and the demand for freshwater (FW), will surely lead to a rise in the prices and spur the use of non-traditional water.

Wastewater (WW) is an untapped resource in a world where FW depletion rates are unprecedented. Yearly, 40 million hectares or 15% of all irrigated lands can be irrigated with the 330 km³ (267.5 million acre-feet/year) municipal wastewater produced around the world (Mateo-Sagasta et al., 2015). Treated wastewater (TWW) has been gaining attention around the world especially in the agriculture community. The population increase is causing a rise in demand for FW for domestic purposes which leads to higher wastewater generation as a result of water usage. TWW has become high

valued due to quality water shortage in many dry areas of the world. TWW could be used to alleviate or prevent further exhaustion of the natural FW resources in the underlying aquifer by helping overcome the shortages and mitigating the severe impact of drought. Irrigation with TWW has been successfully applied in several countries around the globe. In addition, TWW contains nutrients which could replace fertilizers and soil conditioners (Jimenez-Cisneros, 1995; Qadir et al., 2007). Therefore, when TWW is used, resources can be conserved through the potential reduction in fertilizer usage. The Water-Energy-Food nexus concept is addressed in this study, while saving valuable FW and energy, crops are being produced at a regular or even superior rate.

The first use of "sewage" in Texas for irrigation can be traced back to the late 1890s in the region of south San Antonio. In the 20th century, the use of treated effluent water became common in the arid parts of the state mainly in the west, in cities such as Lubbock, Amarillo, Odessa, and Abilene (Texas Water Development Board (TWDB), 2011b). Although, it accounts for a small percentage (2%), water reuse has become a part of the contemporary Texas water portfolio for agriculture (Figure 1).

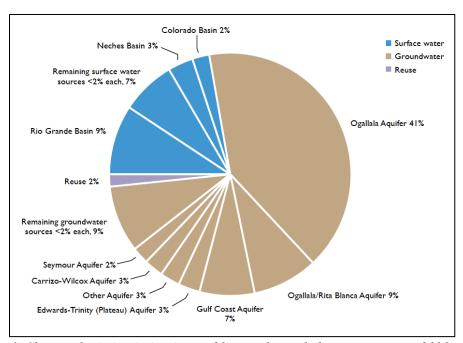


Figure 1: Shares of existing irrigation and livestock supply by water sources 2020 reprinted from TWDB, 2017

Brackish groundwater contains dissolved solids ranging from 1,000 to 10,000 parts per million (ppm) (Table 1). Desalination methods are expensive and produce highly saline concentrate better known as brine. Therefore, the saline groundwater is used for irrigation without any treatment. Farmers tend to prefer irrigating with any sort of water, over rain-fed agriculture as it provides them with better yields because a specific volume of water is necessary for agriculture production (Smedema & Shiati, 2002), but irrigation might not always be the best economic alternative.

Water Class	Total Dissolved Solids (ppm)
Fresh	<1,000
Slightly Saline (Brackish)	1,000-3,000
Moderately Saline (Brackish)	3,000-10,000
Highly Saline	>10,000
Seawater	≈35,000
Brine	>100,000

Table 1: Classification of water based on TDS reprinted from Stanton et al., 2017

The state of Texas has a massive BGW reserve occurring in almost all of its 30 aquifers. According to a study done by LBG-Guyton Associates in 2003 for TWDB, the estimated amount of BGW is more than 2.7 billion acre-feet (acft) widespread within the major and minor aquifers (LBG-Guyton Associates, 2003). Figure 2 shows the extent of the BGW aquifers in Texas.

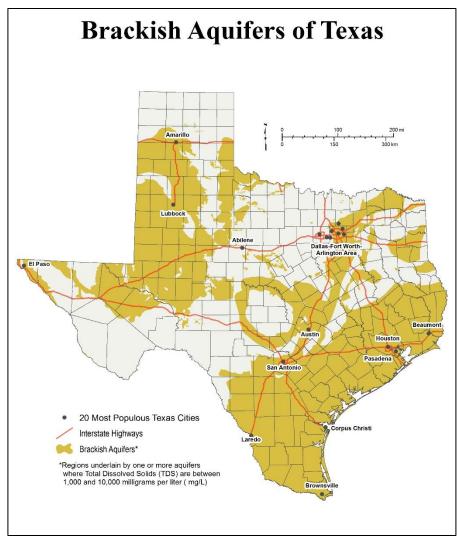


Figure 2: Major and minor brackish aquifers of Texas adapted from LBG-Guyton Associates, 2003

The two unconventional water sources are abundantly available and used on a regular basis in Texas especially in the arid and semiarid lands of the West. The main concern is the soil salinization which has been studied extensively because it has the ideal conditions (evapotranspiration>precipitation + irrigation water) for this issue to occur. Any agricultural land is susceptible to salinization because crops use the water

(precipitation and/or irrigation) and the salts are left behind in the soil to accumulate. When farmers opt to irrigate with TWW and BGW, they become more vulnerable because these sources contain higher levels of salts. While most of the previous studies on irrigation with non-traditional water have mainly targeted the physicochemical alterations of soils, very few studies have been conducted on the modifications of clay minerals.

## 1.2 Objectives

The aim of this study is to address the following research question: Does the long –term application of unconventional water (BGW or TWW) have any impact on soil chemistry and clay mineralogy? In the long run, the use of alternative water (BGW or TWW) will not cause any changes to soil mineralogy, but it will affect the chemistry of the soil compared to rainfed (RF) practices. While keeping in view the importance of alternative water sources and soil health, this study was conducted to address two objectives:

- 1. Quantify the changes that may occur in the chemical properties of the clayey soil.
- 2. Assess the response of the soil's clay mineralogy.

#### 1.3 Literature Review

Reclaimed water has attracted farmers due to its promising fertilizing ability which helps grow crops and improve soil quality and productivity (Environmental Protection Agency (EPA), 2004; Hanjra et al., 2012; Bedbabis et al., 2014). In a study on the impact of TWW on grape yields and quality, the drip irrigation with treated municipal water has increased grape production with no adverse effect on the soil

(Mendoza-Espinosa et al., 2008). Furthermore, the main benefit is the reduction of FW demand from the worldwide highest consumer: the agriculture sector (70%) (FAO, 2010).

Conversely, some researchers rejected the replacement of FW by TWW as a result of increasing salinity causing a degradation in the soil's physical properties (Klay et al., 2010; Hasan et al., 2014). Qian and Mecham have studied the effect of long term application of TWW on golf courses which resulted in soil salinity increase because of the present higher salinity in the reclaimed water (Qian & Mecham, 2005).

Consequently, the most common problem in arable land is soil salinization specifically in arid and semi-arid areas where precipitation is insufficient to prevent salt accumulation which leads to yield reduction (Francois & Maas, 1994; Munns, 2002). However, in semiarid regions with annual precipitation higher than 20 inch, the rain is sufficient to prevent long-term salt accumulation in the root zone in areas irrigated with secondary TWW (Lado et al., 2012). The scholars that argue that using recycled water for irrigation harms soil health attribute this negative effect to the water chemistry.

Public health and safety are among the major issues with applying marginal quality water where it is mostly employed in countries with unenforced regulations. In developed countries such as the United States, the use of TWW is regulated through governmental (US Environmental Protection Agency) and local agencies. In the "Lone Star State", there are constraints set by the Texas Commission on Environmental Quality (TCEQ) for the use of treated wastewater. Reclaimed water is classified into two types: Type I and Type II (Table 2). The end use of the categories differ because of the quality

of each type. Type I could be applied where public contact is likely but Type II is restricted to areas where human contact is unlikely. Therefore, any health risks are minimized to non-existent.

	Type I	Type II
Quality Standards (30 day average)	<ul> <li>BODs/CBODs = 5 mg/L</li> <li>Turbidity = 3 NTU</li> <li>Fecal coliform &lt; 20 or &lt; 75 CFU/100 mL (single grab)</li> </ul>	<ul> <li>BODs = 20mg/L</li> <li>CBODs = 15 mg/L</li> <li>Fecal coliform &lt; 200 or &lt; 800 CFU/100 mL (single grab)</li> <li>For a pond system: BODs = 30 mg/L, Fecal coliform &lt; 20 or &lt; 800 CFU/100 mL (single grab)</li> </ul>
Sampling/Analysis Frequency	Twice per week	Once per week

Table 2: Water quality parameters for using reclaimed water adapted from 30 Tex. Admin. Code § 210.33-210.34

Generally, wastewater has a higher concentration of salts and nutrients compared to traditional water resources which raises another issue when used for irrigation resulting in accumulation of salts in the soil profile (Table 3).

CONCENTRATION (ppm)				
CONTAMINANTS	LOW	MODERATE	HIGH	
Solids, total	350	720	1200	
Dissolved, total	250	500	850	
Volatile	105	200	325	
Suspended solids	100	220	350	
Volatile	80	164	275	
Settleable solids	5	10	20	
BOD (5-day,20°C)	110	220	400	
TOC	80	160	290	
COD	250	500	1000	
Nitrogen (total as N)	20	40	85	
Organic	8	15	35	
Free Ammonia	12	25	50	
Nitrites	0	0	0	
Nitrates	0	0	0	
Phosphorus (total as P)	4	8	15	
Organic	1	3	5	
Inorganic	3	5	10	

Table 3: Typical composition of untreated domestic wastewater reprinted from Pepper, Gerba & Brusseau, 2011

The quality of reclaimed water ultimately depends on the source of wastewater and the adopted treatment method. Municipal wastewater is generated from households, business and commercial establishments, and sometimes industrial facilities. Domestic wastewater has a lower salinity relative to industrial wastewater (Hamilton et al., 2007; Gómez-Bellot et al., 2014). The main goals of wastewater treatment systems is to reduce biological oxygen demand (BOD₅) and suspended solids. TWW can be used for agriculture because it is generally clean enough, nevertheless it contains higher (≈1.5 times) concentrations of dissolved solids than the source water (Pepper, Gerba & Brusseau, 2011). The removal of salts is not achieved by conventional WW treatment processes provided by most reclamation facilities because it is expensive, energy

consuming, and salt concentrations are not regulated (Toze, 2006; Mosse et al., 2011). Therefore, the irrigation with TWW is considered to be of concern because of the existence of elevated levels of specific monovalent cations (Na<sup>+</sup> and K<sup>+</sup>) which can degrade the soil structure. Sodium and potassium cations are characterized by being single charged and having a large hydrated radii resulting in poor flocculation abilities. High concentrations of these ions would displace the good flocculators which are divalent magnesium and calcium cations. Furthermore, the presence of Na<sup>+</sup> in exchangeable positions increases the plasticity of clay and can make the soil containing such clays unsuitable for agriculture. The stabilization of aggregates is effectively achieved by divalent cations, because of their larger charge density and ability to crosslink colloids (Laurenson et al., 2012). A healthy soil needs to be flocculated for water to infiltrate. In opposition, the physical structure of the soil would be damaged when clays swell and disperse because of the deficit in calcium and magnesium (Ca<sup>2+</sup> and Mg<sup>2+</sup>) ions (Rengasamy and Marchuk, 2011). Experiments on soil permeability using single cation solutions have concluded that Ca<sup>2+</sup> sustains permeability and Na<sup>+</sup> decreases it (Quirk and Schofield, 1955). However, a study in Australia on the relative effects of Na<sup>+</sup> and K<sup>+</sup> on a smectitic clay soil using solutions with 5-40 range of sodium adsorption ratio (SAR) showed that low SAR values of 5 had an insignificant impact on the hydraulic conductivity of the soil (Arienzo et al., 2012). The ideal conditions for healthy soils is to have clay minerals containing a mixture of Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup> as exchangeable cations.

Saline water has captured attention especially in arid regions where FW is scarce (Mushtaq & Moghaddasi, 2011). BGW has been used for irrigation with success and proved to be helpful for growing and producing crops. In a study of 8-years of field experiments where BGW was used for irrigation of winter wheat and maize, the authors established that irrigating with slightly brackish water was the most beneficial irrigation scheme although FW is needed for leaching the accumulated salt when precipitation events are rare (Ma et al., 2008). Some researchers have showed the promising potential of brackish water irrigation, specifically in the dry season, in climatic conditions with an average annual rainfall of 15in-24in where the salt that accumulated during the former period is leached with the rain (Hamdy et al., 2005; Kiani & Mirlatifi, 2012). The main issue with BGW is the salt build-up in the soil which can be harmful for sensitive crops (Rengasamy, 2010; Ramos et al., 2012; Wang et al., 2015). However, BGW can be used and salt accumulation can be avoided, by means of a proper irrigation schedule. The main crop in the area of interest is cotton which is an excellent product because it is a highly salt tolerant crop with a soil of 7.7 deci-Siemens per meter (dS/m) EC threshold (Bernstein & Ford, 1959) and it is Texas's most valuable crop leading the country with a \$1.6 billion in cotton and cottonseed sales (United States Department of Agriculture (USDA), 2015).

Several components could influence the soil's functions but its texture and mineralogy dominate the reaction to unusual additions such as irrigating with TWW or BGW. The impact of marginal water quality on soils differs depending on the clay content and mineralogy, particle surface charge characteristics, pH, and organic matter

content (Huang et al., 2012). Researchers argue that sodic conditions are more likely to occur in soils with a higher clay content (Leal et al., 2009; Chen et al., 2013). Also, irrigation methods play a key role in the soil chemical properties modifications that might occur when applying recycled domestic water (Maas and Grattan, 1999; Malash et al., 2007) and saline water (Kang et al., 2010; Zhao et al. 2015).

The change in clay mineralogy in soils over a short period as a result of anthropogenic actions such as irrigation with TWW or BGW has rarely been documented. Furthermore, it has been thought that such alterations could only occur over geological time scales. The smectite illitization can occur over a short time period (Barré et al., 2008). Although, burial diagenesis is the most common for the conversion to occur but this process can happen at or close to the Earth's surface in the upper horizons of soils under very different environmental conditions such as low pressure and temperature. Therefore, the phenomenon can transpire in geological and artificial settings especially where high pH K-solutions are present (Drief, 2002). Time, chemical composition, and temperature are the major components for this transformation to go through. K-rich raw wastewater from a winery was applied to Australian clayey soils where smectite minerals were altered to form interstratified illite and smectite minerals and changed poorly crystallized illite to a well-organized form (Marchuk et al., 2016). Treated wastewater might meet the description of the conditions needed for smectite to transform into illite in a pedogenic setting. On the other hand, some studies have found no significant effects on soil mineralogy composition due to the long term irrigation with TWW (Tarchouna et al., 2010; Rezapour & Samadi, 2011).

#### 2. MATERIALS AND METHODS

# 2.1 Overall Approach

The study was carried out from January to October 2017 in an area that was chosen on the basis of the long term use of TWW for irrigation and the scarcity of FW sources. Figure 3 outlines the general procedure of this work. The Web Soil Survey tool from the Natural Resources Conservation Service (NRCS) was used to determine that the Angelo series is the dominant soil series of the study area ("Web Soil Survey -Home", 2017). The Angelo soils are fine-silty, mixed, superactive, thermic Aridic Calciustolls. The Angelo series consists of deep or very deep, well drained, moderately slowly permeable soils formed in calcareous loamy and clayey alluvium derived from limestone. The Angelo series occupies 23.4% of Tom Green County prevailing over the rest of the soils. Furthermore, Angelo clay loam, 0 to 1 percent slopes (AnA) is the main mapping unit from the Angelo series covering 16.2% of the county (Wiedenfeld & Flores, 1976). Water samples were collected, using 16-oz plastic bottles, from the different sources that are used for irrigation. The chemical analysis of the water samples was performed at Texas A&M University Soil, Water, and Forage Laboratory in College Station. In total, 10 different soil samples were taken from the three top horizons of the different fields except the filter-flush (FF) where the Ap horizon was sampled only. The samples were obtained by a trowel and were placed in gallon Ziplock bags and were airdried. The RF field is used as a control since it has not been irrigated and the FF was sampled because it portrays an intensive case of TWW irrigation. The texture, chemical,

and mineralogical properties of the soil were investigated at the Heep Center in Texas A&M University. After all the data was obtained, it was analyzed to answer the hypothesis and complete the objectives.

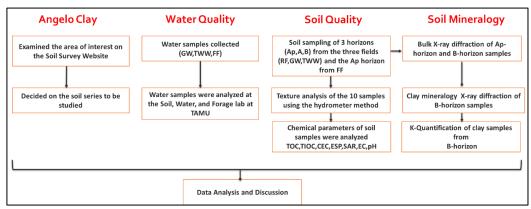


Figure 3: Chart summarizing the methods

## 2.2 Study Area

The location of the area of interest was in a rural setting of Tom Green County, in West Central Texas (Figure 4). The area is located in the southeast portion of the city of San Angelo. The irrigation system used in this study is drip irrigation where TWW has been applied to irrigate cotton for more than 10 years which could have led to changes in the soil's chemistry. The cotton farm is divided into three agriculture practices with most of the land being irrigated (Table 4). The region is classified as semi-arid according to its average annual precipitation of 21.25 inch but it is on the edge of being classified as humid temperate because of its considerably high humidity ("West Central Texas Climate Data", 2017). The fluctuation of the weather adds more pressure

on farmers receiving less water input from rain. The city of San Angelo is located on top of the Lipan Aquifer (Figure 5) which is considered to have high available BGW and very shallow with a moderately transmissive alluvial stratigraphy. The aquifer holds approximately 1.3 million acft with most of the water ranked as slightly saline (LBG-Guyton Associates, 2003). Since 1958, the city of San Angelo disposed of primary treated municipal wastewater onto agricultural land as solution to the marginal quality water. Municipal wastewater had to be treated further in order to decrease water pollution as enacted on October 18, 1972 by the Clean Water Act (Public Law 92-500). By 1983, all wastewater treatment facilities owned by the government were required to meet the secondary treatment effluent standard (Water Pollution Control Act, 1972). As a result, the reclamation plant in San Angelo upgraded to secondary treatment by an activated sludge process. Currently, the treated effluent water is seen as a solution to cope with demographics and the harsh climate in order to meet irrigation requirements. According to the Texas Water Development Board's (TWDB) 2017 State plan, in 2020 San Angelo will be using 8300 acft of TWW for irrigation purposes (TWDB, 2017).



Figure 4: Location of the study area

Agricultural Practices	Size (acres)
Dryland/Rainfed	70
BGW Drip Irrigation	115
TWW Drip Irrigation	250

Table 4: Size of the different agriculture practices

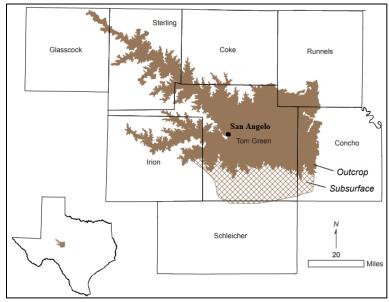


Figure 5: Lipan aquifer modified from TWDB, 2011a

# 2.3 Water Sampling and Analysis

The wastewater is treated to Type II standards regarding the Texas Commission on Environmental Quality (TCEQ) regulations (30 Tex. Admin. Code §210.33) by the water reclamation facility in San Angelo before arriving to holding lagoons for further treatment and finally sent out to contracted farmers for use (Table 5).

Type II reclaimed water use, for a system other than pond system				
BOD <sub>5</sub>	20 mg/l			
or CBOD <sub>5</sub>	15 mg/l			
Fecal coliform or E. coli	200 CFU/100 ml*			
Fecal coliform or E. coli	800 CFU/100 ml**			
Enterococci	35 CFU/100 ml*			
Enterococci	89 CFU/100 ml**			
*30 day geometric mean ** maximum single grab sample				

Table 5: Minimum water quality of Type II reclaimed water adapted from 30 Tex. Admin. Code \$210.33

The composition of the wastewater changes even on a local scale depending on the source. The most common source for previous studies has been treated municipal effluent. Moreover, in prior research the TWW always had higher salinity levels compared to the local water source used to run the experience. In this work, the case is reversed because the groundwater (GW) quality in the alluvial Lipan aquifer was degraded via anthropogenic and natural sources of salinity (Ashworth & Hopkins, 1995). The water quality starts to decline at the top of the Permian formations (Figure 6 & Table 6), it becomes very hard and is considered to range from marginally fresh to moderately saline (Lee, 1986).

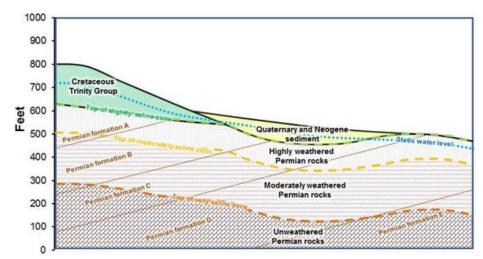


Figure 6: Formation salinity schematic reprinted from TWDB, 2017

	Depth below ground (feet)		
Geological formation	3,000 mg/L	10,000 mg/L	
Yates Formation	190	390	
Seven Rivers Formation	150	500	
Queen Formation	0	660	
San Angelo Formation	160	770	
Upper Choza member	190	310	
Tubb member	270	330	
Bullwagon Dolomite	190	240	
Arroyo Formation	180	240	
Lueders Formation	150	220	
Average	164	362	

Table 6: Salinity zone determination by formation reprinted from TWDB, 2017

The treated wastewater used by the farmer was sampled from the man-made canals where the water is held before it is pumped for irrigation (Figure 7). The BGW was sampled from three different wells present on the land. Well B is the most representative of the water used for the BGW irrigated soils for this study (Figure 8).



Figure 7: Man-made canal holding treated wastewater



Figure 8: Water sampling location

Additionally, the sampling for the FF water was done from the ponding caused by the pipe that dumps out the backflush water from the filter flush system. The Arkal Spin Klin is a modular, automatic, self-cleaning, polymeric disc filter that is highly suitable for corrosive water application (Figure 9). Furthermore, it captures suspended solids from the water with a size of 130 micron or larger, then the filtered water is sent to the drip system for irrigation. The accumulation of particulates on the filter causes the buildup of pressure that triggers the pressure sensor and activates the self-cleaning process. The filters are flushed by TWW and the highly concentrated water is pumped out by an automatic backflush system. The FF water is full of suspended solids and was sampled as a concentrated TWW. The routine water analysis was carried out by the lab at Texas A&M University using standard methods such as inductively coupled plasma, titration, ion selective electrode, and cadmium reduction. The analysis included the following tests: electroconductivity (EC), pH, sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), carbonate (CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub>), sulfate (SO<sub>4</sub>), chloride (Cl), boron (B), nitrate (NO<sub>3</sub>-N), phosphorus (P), total dissolved salts (TDS), Alkalinity, Hardness and SAR.



Figure 9: Arkal Spin Klin filter

# 2.4 Soil Sampling and Physicochemical Parameters Analysis

After determining the major soil series in the area, the three soil horizons (Ap, A, and B) from the AnA were sampled from three different fields: RF, BGW irrigation, TWW irrigation. In addition, the Ap horizon was sampled from the FF field to be used as an accelerated effect of TWW irrigation (Figure 10). The fields are drip-irrigated with the drip rows at 12-14 inch deep.

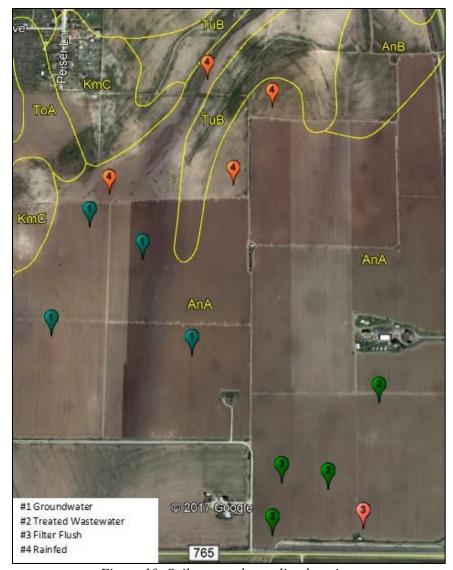


Figure 10: Soil map and sampling locations

The physicochemical and mineralogical parameters of the soils were analyzed in the Soil and Crop Sciences Department at Texas A&M University. The texture of the soil was analyzed by the hydrometer method (Gee & Bauder, 1979). The CEC was figured out by potassium saturation, the exchangeable bases (Ca, Mg, and Na) were determined by ammonium acetate (NH<sub>4</sub>OAc) extraction, exchangeable sodium

percentage (ESP) and exchangeable sodium ratio (ESR) were calculated based on the exchangeable cations data (EQ.1 and 2). The saturated paste method was used to determine the EC, soluble cations, and pH. The SAR was calculated using EQ.3 based on the soluble cations. The Gapon equation that shows the relationship between ESR and SAR is demonstrated in Eq.4 where X is the soil, the exchangeable ion concentrations are in millimoles (+) per kilogram and  $K_G$  is the Gapon exchange constant ranging from 0.010 to 0.015 (L mmol)<sup>-1/2</sup> (Stewart and Lal, 1992).

EQ.1 
$$ESP (\%) = 100 \times \frac{[Na]^+}{[Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]}$$

EQ.2 
$$ESR = 100 \times \frac{[Na]^+}{[Ca^{2+}] + [Mg^{2+}]}$$

EQ.3 
$$SAR = \frac{[Na]^+}{\sqrt{\frac{[Ca^{2+}]+[Mg^{2+}]}{2}}}$$

EQ.4 
$$ESR = \frac{[NaX]^{+}}{[CaX + MgX]} = \frac{K_G[Na^{+}]}{[\frac{[Ca^{2^{+}} + Mg^{2^{+}}]}{2}]^{1/2}} = K_GSAR$$

# 2.5 Soil Clay Mineralogy Analysis

The overall mineralogy of the soil was examined by performing a bulk X-ray diffraction (XRD) on the B-horizons of the different fields (TWW, BGW, and RF). Bulk XRD provides an initial survey of the whole sample (sand, silt, clay). Then, powder XRD was used to identify clay minerals in the soil. The B-horizon has the highest clay content and the lowest erosion compared to A and Ap because it is the deepest.

Therefore, if any mineralogical changes have occurred with the introduction of TWW or BGW it would appear in the deepest horizon. The clay was separated from sand by sieving and from silt by size by centrifugation method which is based on Stokes' Law. A

clean and dry clay sample was obtained after dialysis of the condensed clay suspensions from the centrifugation procedure in order to remove any surplus of electrolytes.

Afterwards, the clay samples were oven-dried at 60 °C and finely grounded for XRD analysis. The clay fractions were further treated, some subsamples were saturated with Mg and K. Additionally, after the first diffraction pattern of the Mg saturated sample, it underwent a glycerol treatment to aid in the detection of smectite. Also, the K treated subsample underwent several heat treatments in order to detect kaolinite and mica. The final procedure for clay samples was quantification of mica by total K determination.

Using the HF method (acid dissolution technique) which is a modification of the Bernas (1968) method. The used method measures the solutions and clay sample directly into a Nalgene volumetric flask allowing the digestion to continue occurring at room temperature.

#### 3. RESULTS AND DISCUSSION

## 3.1 Characterization of the Irrigation Water

The results from the inorganic chemical analysis of the groundwater samples are shown in Table 7 and the data for all the water used for irrigation in the study area are represented in Table 8. The GW wells increase in depth going from A to C which led to the rise of salinity levels as a result of penetrating deeper formations (Figure 6). The treated wastewater in the study area differs greatly from the groundwater for many reasons. First, the sodium (Na) concentration for BGW is higher than 400 ppm which is recommended for irrigation water (Provin and Pitt, 2002), therefore it may lead to significant burning of the foliage. In addition, the high Na concentration in irrigation water may cause poor soil structure as a result of sodicity in the soil. Second, the chloride (Cl<sup>-</sup>) levels for BGW are very high and exceed the suggested concentration for maximum Cl<sup>-</sup> content (900 ppm), the water is considered unsuitable for all agronomic crops as it inhibits plants growth by reducing phosphorus availability (Provin and Pitt, 2002). Third, the sulfate (SO<sub>4</sub><sup>-</sup>) concentration for the BGW is higher than the recommended levels by FAO (Table 8) which could cause the same effect as Cl<sup>-</sup> for plants and leads to potential acidification of the soil. BGW and TWW have high TDS, but the former's salinity (moderately saline) is more than triple of TWW (slightly saline) which increases the risks of damaging the soil and plants by salt accumulation. The TWW and FF have similar water chemistry because TWW is used as the backflush for the FF system. Water quality with EC higher than 3.0 dS/m and TDS above 1,920 means high salinity hazard, the water is generally unacceptable for irrigation, except for very salt-tolerant plants where there is excellent drainage, frequent leaching, and intensive management (Provin and Pitt, 2002). The main crop in the study area is cotton which can handle water with EC up to 5.1 dS/m without yield reduction (Ayers and Westcot, 1976). In the case of BGW, reduction of yield occurs at a rate of approximately 20% as stated by the farmer in the area of interest. Excess salts from water accumulate in the soil and increase the osmotic pressure of the soil solution leading to plant wilting. In addition, the farmer claims that the yield from TWW irrigation is around 3.5-4 bales per acre compared to 3 bales for BGW and ¾ bales for RF.

In summary the TWW has a much better quality and provides higher yields compared to the groundwater for the reasons discussed above. Furthermore, as a result of the high salinity levels, BGW could prove detrimental to the soil and crop yields (Halliwell et al., 2001).

Parameters	GW A	GW B	GW C
Depth (ft)	120	230	280
pН	6.73	7.09	6.98
EC (dS/m)	6.93	7.02	7.595
Hardness (ppm CaCO3)	2330	2671	2900
Alkalinity (ppm CaCO3)	176	177	187
SAR	4.3	4.2	4.2
Calcium (ppm)	618	739	803
Magnesium (ppm)	191	200	218
Sodium (ppm)	479	495	514
Potassium (ppm)	6	8	8
Boron (ppm)	0.32	0.365	0.49
Bicarbonate (ppm)	215	215	228
Sulfate (ppm)	910	1280	1006
Chloride (ppm)	1306	1339	1701
Nitrate-N (ppm)	34.35	34.61	41.52
Phosphorus (ppm)	0.07	0.07	0.07
Total Dissolved Salts (ppm)	3760	4312	4520

Table 7: Depth and Chemical characteristics of the different groundwater wells

Parameters	TWW	BGW (GW B)	FF	Irrigation Water Quality Criteria (FAO, 1985)
pН	7.7	7.09	8	6.5-8.5
EC(dS/m)	2.135	7.02	2.455	3
Hardness (ppm CaCO3)	454	2671	503	-
Alkalinity (ppm CaCO3)	241	177	227	-
SAR	4.7	4.2	5.2	12-20
Calcium (ppm)	101	739	111	400
Magnesium (ppm)	49	200	55	60
Sodium (ppm)	229	495	266	920
Potassium (ppm)	25	8	29	2
Boron (ppm)	0.49	0.365	0.55	3
Carbonate (ppm)	0	0	3	-
Bicarbonate (ppm)	295	215	271	610
Sulfate (ppm)	212	1280	262	960
Chloride (ppm)	431	1339	516	355
Nitrate-N (ppm)	11.06	34.61	3.65	40
Phosphorus (ppm)	2.5	0.07	1.25	5
Total Dissolved Salts (ppm)	1356	4312	1518	2000

Table 8: Chemical characteristics of the water used for irrigation

# 3.2 Impact on Soil Physicochemical Parameters

The chemical characteristics and texture of the different horizons are documented in Table 9. The high CEC values observed in all the samples could be attributed to the high clay content and the organic carbon of the soil. The EC values of the irrigated soils are marginally higher compared to RF soils because the irrigation water introduces soluble salts to the soil. Furthermore, the highest EC value was in the FF soil (Figure 11)

because the water is highly concentrated with salts and the soil is rarely surface flood irrigated by the FF system. The SAR values follow a similar trend with a marginal rise in the irrigated soils (Figure 12). However, in this case TWW soils have higher SAR numbers than BGW irrigated soils as a result of the TWW having a higher Na<sup>+</sup> concentration compared to Ca<sup>2+</sup> concentration (Table 8). Figure 13 shows the ESP response of the soils, and the results are following the same trend as the SAR. The ESR in the soils and SAR in the extracts (soluble cations) are highly correlated which further solidifies the accuracy of the data (Figure 14). According to the Natural Resources Conservation Service (NRCS), a soil is classified as sodic when pH is above 8.5, SAR and ESP are greater than 13 and 15 respectively. In the case of the Angelo series samples all the values of interest (SAR, ESP, and pH) are low indicating no sodicity problems (Table 10). Saline soils are characterized by having an EC greater than 4 dS/m, all the samples have low numbers which means salinity problems are not an issue for this soil and the cotton crop (Table 10). The situation is ideal because the main crop in the study area is cotton which has a high salt tolerance (Maas and Hoffman, 1977). The TOC slightly increases as a result of TWW and BGW application because irrigation increases yields resulting in high organic material deposited on the soil from the crops compared to RF agriculture (Figure 15). The FF irrigated soil has the highest TOC because it contains all the materials filtered from TWW (Figure 15).

In summary, soil salinization was not a factor after 14 years of irrigation with TWW nor irrigation with BGW.

Angelo Cl	ay Loam					Parameters														
						Concentration in Saturated Extract			Exchangeable Cations											
						EC	K	Na	Ca	Mg	SAR	К	Na	Ca	Mg	CEC	ESR	ESP	ОМ	TOC
Soil	Depth (cm)	Clay Content (%)	Texture	рН		dS/m (mmol(+)/L)		cmol(+)/kg						%	9	6				
RF Ap	0-15 33.40	22.40	Clay Loam	17.52	Mean	0.47	0.49	0.62	4.53	0.31	0.58	1.08	0.28	38.63	1.84	43.69	0.69	0.67	3.39	1.73
нг Ар	0-13	33.40			SD	0.19	0.41	0.39	1.26	0.54	0.47	0.32	0.04	5.84	0.74	4.55	0.05	0.05	0.63	0.32
RF A	15-30	42.92	Clay	7.41	Mean	0.60	1.03	0.62	5.61	0.29	0.50	0.95	0.31	39.89	1.82	46.31	0.74	0.72	3.53	1.80
IN A	15-50	42.52			SD	0.17	1.28	0.25	1.27	0.49	0.25	0.23	0.03	5.42	0.82	5.36	0.02	0.02	0.49	0.25
RF B	30-72	49.68	Clay	7.17	Mean	0.97	0.41	1.38	9.66	0.30	0.99	0.73	0.43	39.66	1.89	45.91	1.01	0.98	3.38	1.72
111 5	30-72	45.00			SD	0.59	0.30	0.72	7.86	0.51	0.48	0.14	0.16	4.60	0.85	4.26	0.28	0.27	0.67	0.34
BGW Ap	0-15	35.26	Clay Loam	7.59	Mean	1.43	1.05	1.68	11.61	0.59	0.89	1.74	0.40	39.86	3.30	48.08	0.93	0.88	4.15	2.12
БОТТ АР	0-13	33.20			SD	0.33	0.13	0.53	1.90	0.98	0.29	0.18	0.06	3.50	0.71	3.12	0.09	0.08	0.48	0.25
BGW A	15-30	45.31	Clay	7.38	Mean	1.02	0.61	0.86	7.78	0.65	0.68	1.27	0.40	39.92	2.93	48.33	0.92	0.89	4.35	2.22
DOWA	15-50	45.51			SD	0.58	0.37	0.44	3.57	1.11	0.41	0.37	0.10	2.89	0.67	3.48	0.19	0.18	1.00	0.51
BGW B	30-72	49.52	Clay 7.	17.331	Mean	1.13	0.38	3.66	6.47	1.27	1.89	1.03	0.75	39.73	3.52	49.22	1.70	1.63	4.47	2.28
DOW D	30-72	45.52			SD	0.97	0.20	4.02	4.65	2.20	0.88	0.33	0.44	2.22	0.82	2.47	0.90	0.85	0.47	0.24
TWW Ap	0-15	47.17	Clay	17.52⊢	Mean	1.69	1.71	5.27	8.91	2.49	3.74	1.88	0.84	36.55	5.41	47.33	2.01	1.89	4.26	2.17
	0 10	17.127	City /		SD	1.19	1.86	3.23	8.13	4.29	2.74	0.22	0.27	3.00	1.27	1.59	0.68	0.63	0.26	0.13
TWW A	15-30	50.90	Clay	7.61	Mean	2.33	0.82	9.92	10.24	0.59	5.20	1.53	1.15	37.39	5.81	50.02	2.71	2.53	4.02	2.05
	25-50	33.30			SD	2.03	0.27	9.31	8.30	0.95	3.58	0.29	0.60	3.00	1.47	1.77	1.47	1.35	0.24	0.12
TWW B	30-72	54.51	Clav	7.66	Mean	1.79	0.56	8.11	6.83	0.54	5.35	1.18	1.29	36.72	5.94	48.82	3.02	2.84	3.54	1.80
	30-72	J4.J1 Clay	c.uy		SD	0.77	0.10	4.07	2.95	0.87	2.41	0.33	0.39	3.27	1.29	1.47	0.90	0.81	0.23	0.12
FF	0-15	48.15	Clay	7.46		3.5	1.86	12.85	11.57	4.20	4.57	1.33	1.86	39.86	4.68	52.00	4.17	3.89	4.99	2.54

Table 9: Physiochemical and Mineralogical Properties of the Soil

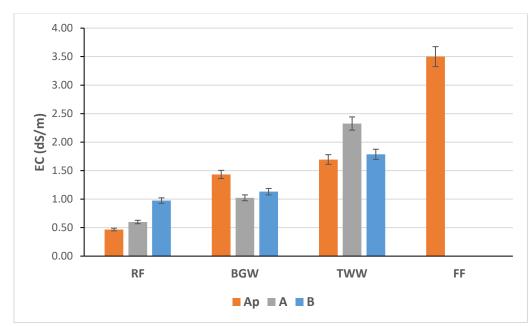


Figure 11: Electroconductivity of the different soils

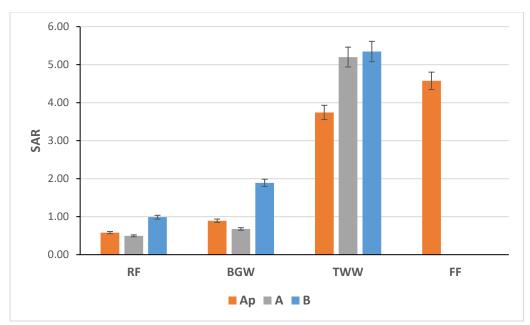


Figure 12: Sodium Adsorption Rate of the different soils

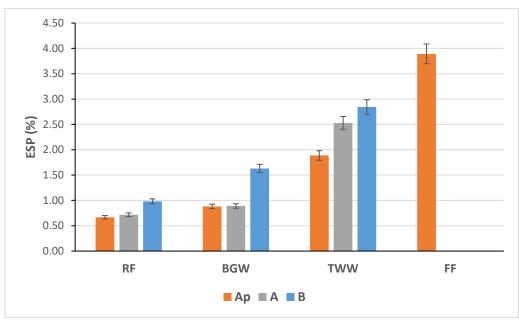


Figure 13: Exchangeable Sodium Percentage of the different soils

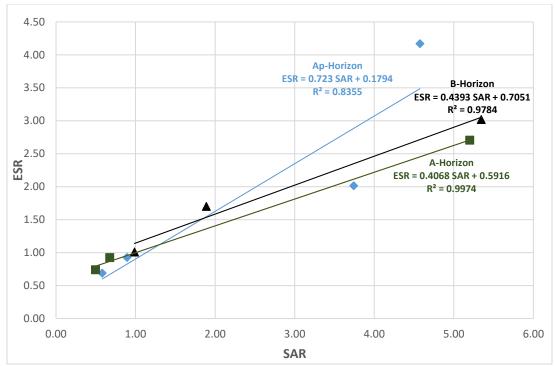


Figure 14: ESR as a function of SAR for of the different soils

Class	EC (dS/m)	SAR	ESP	Typical soil structural condition*
Normal	<4	<13	<15	Flocculated
Saline	>4	<13	<15	Flocculated
Sodic	<4	>13	>15	Dispersed
Saline-Sodic	>4	>13	>15	Flocculated

\*Soil structural condition also depends on other factors not included in the NRCS classification system, including soil organic matter, soil texture and EC of irrigation water (Horneck et al., 2007).

Table 10: Classification of salt-affected soils according to NRCS reprinted from Richards, 1954

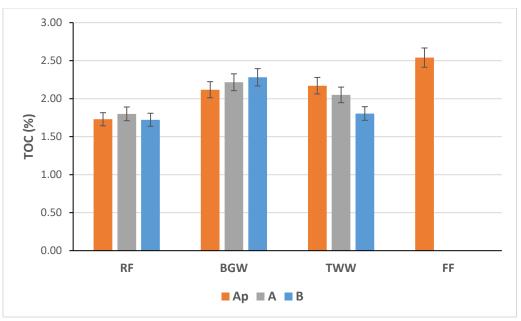


Figure 15: Total Organic Carbon of the different soils

## 3.3 Impact on Soil Clay Mineralogy

The results from the bulk XRD showed identical peaks for the three treatments (Figure 16). The minerals present in the overall samples are quartz (3.34Å), calcite (3.03Å), and minor feldspars (albite and microcline) in between quartz and calcite peaks. The dominant mineral is quartz followed by calcite in the bulk samples. For the powdered XRD (Figures 17, 18, 19), all the samples had similar peaks with intensity and shape alike: Peak at 15.1-15.5 Å on the Mg-saturated XRD pattern slightly collapses upon glycerol solvation indicating a slight random mica-smectite interstratification. Mica is observed in the sample, it is indicated by peaks 10, 5, 3.3 Å. Kaolinite is shown by peaks 7.15 and 3.6 Å. Quartz and calcite are observed at 4.26 and 3.03 Å respectively.

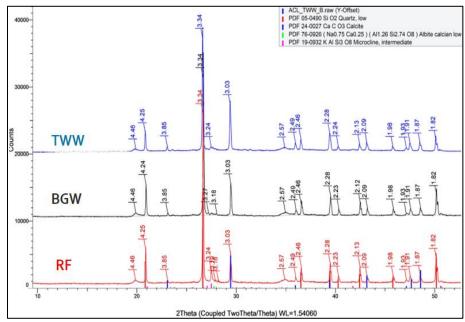


Figure 16: Bulk X-Ray diffraction of the different B-horizons

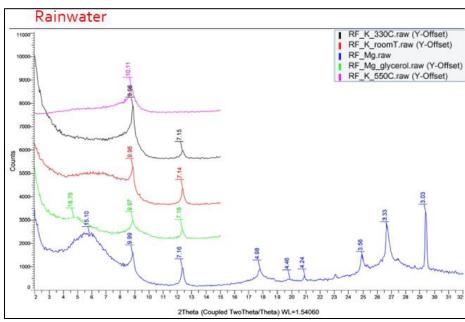


Figure 17: X-Ray powder diffraction of Rain-fed clay sample

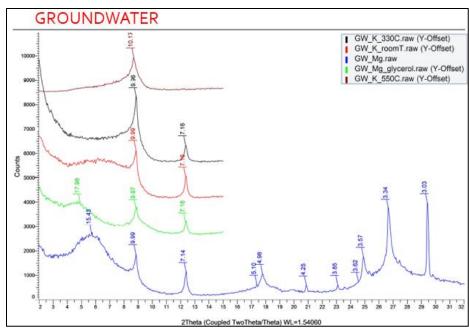


Figure 18: X-Ray powder diffraction of Brackish Groundwater clay sample

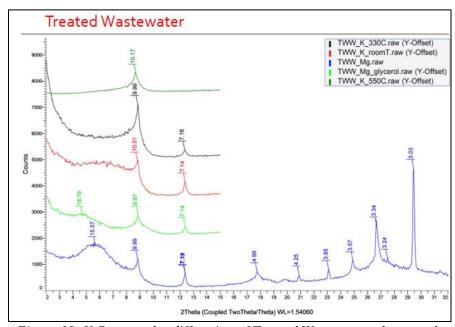


Figure 19: X-Ray powder diffraction of Treated Wastewater clay sample

The K-Quantification technique provided the amount of Mica present in each sample (Table 11). Illite/mica constitutes about 20% of the clay minerals in each sample. Smectite is the dominant mineral, it is assumed that it constitutes around 50% of the clay samples because it has broad peaks with a large surface area and the high CEC shown in the chemical analysis data (Table 8). Furthermore, kaolinite is the least dominant making up around 10% of the clay sample. Each clay sample is composed of approximately 15-18% of calcite depending on the presence of quartz.

Samples	%K	%Mica	Average % Mica				
RF1	1.5	18.1	19.1				
RF2	1.7	20	19.1				
GW1	1.8	21.8	21.2				
GW2	1.7	20.9	21.3				
TWW1	1.6	19.5	10.9				
TWW2	1.7	20.1	19.8				

Table 11: Quantification of Mica in clay samples

To summarize, the soil bulk and clay mineralogy are not altered because the water sources used for irrigation are close to regular conditions and don't hold extreme concentrations of salts. However, the trends of illite percentages are showing that perhaps on a long-run BGW irrigated soils would become richer in illite and decrease in smectite content via Illitization.

## 4. CONCLUSIONS

The use of treated wastewater for agriculture can be traced back to many centuries ago across the world and to the late 19th century in Texas. Reclaimed water use is on the rise as a result of water scarcity that is growing with the population demands. However, a product of the growth in population will be the addition of more wastewater to the channel for use.

This study proved that unconventional water sources (TWW and BGW) are a viable substitute for FW irrigation in semi-arid and arid regions, because there was no significant changes in the soil chemistry nor any sign of salinity or sodicity problems. TWW has a better quality (pH, salinity, chloride, sodium, and sulfate) than the saline groundwater of the Lipan Aquifer. The soil's health is a reflection of the quality of the irrigation water meaning in the long term the BGW could lead to salinity problems. Therefore, TWW should be used instead of BGW to decrease the stress on the Lipan Aquifer that is shared by 8 counties. In addition to the reduction of groundwater pumping, the use of TWW could help the aquifer to replenish properly and could lead to enhancing the groundwater quality. Soils with high clay content, organic carbon, and smectite lead to high CEC values which provides a large nutrient reserve.

Clay mineralogy is stable and plays a major role in the fertility of the soil.

Although, a minor increase (insignificant) in illite content under BGW irrigation was observed but clay mineralogy is not easily changed over a short time period where close

to regular conditions occur. An artificial setting that imitates geological conditions is needed for such a change (High pH K-Solutions, Seawater at high temperatures 50°C...).

Future work should focus on correlating the soil chemistry and clay mineralogy results with the hydrostructural properties of the soil using the pedostructure theory model (Braudeau et al., 2014) and the Typosoil™ apparatus (Assi et al., 2014) to measure continuously and simultaneously the Soil Shrinkage Curve (SSC) and the Water Retention Curve (WRC). Also, the soil microbiology and yields alterations when using TWW compared to BGW and RF agriculture should be evaluated. The chemistry and mineralogy of the soil showed no apparent changes resulting from the use of alternative water sources. Therefore, exploring the other properties of the soil (microbiology and pedostructure) is needed to conclude the overall impact of non-traditional water irrigation. Another beneficial work would be the comparison of Angelo soils irrigated with FW to the soils from this study.

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